Hydride Development for Hydrogen Storage

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Sandia Team

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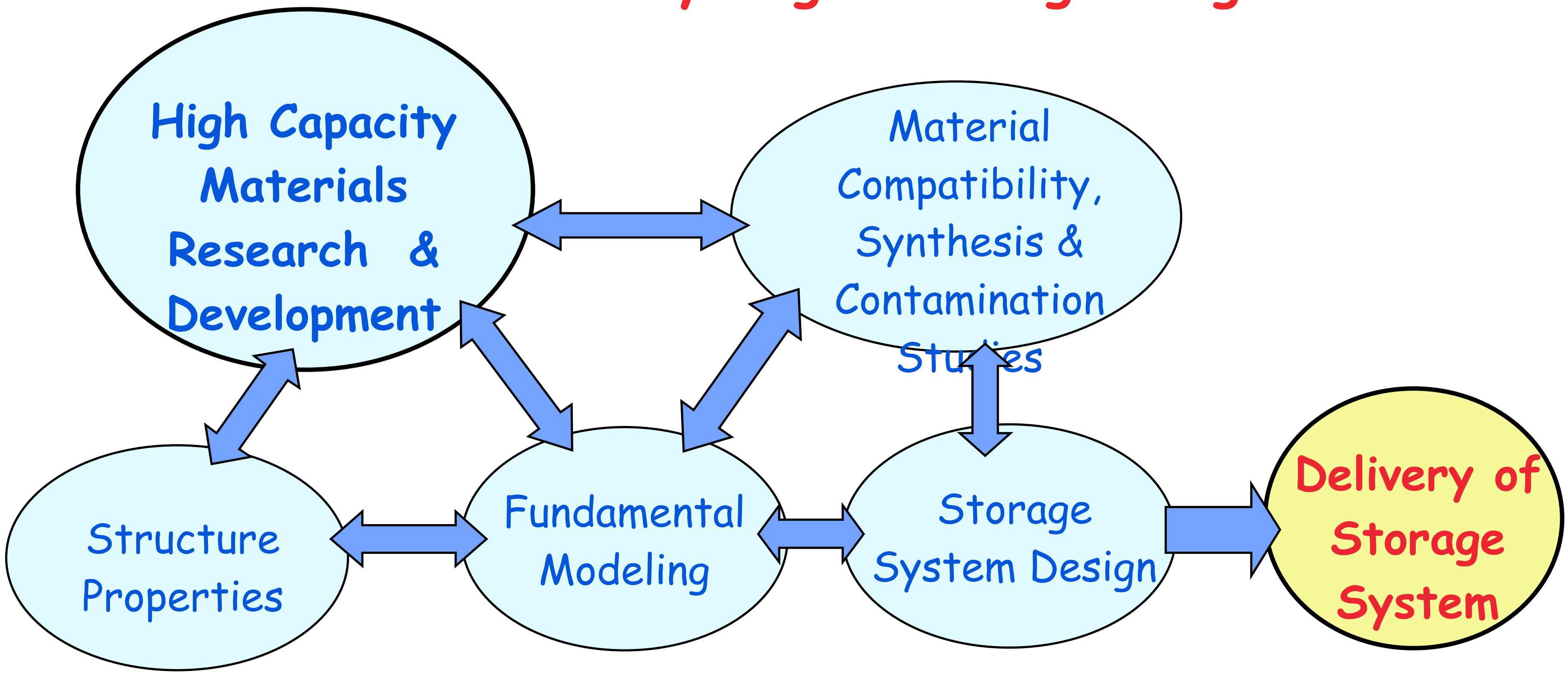
Jay Keller	Gary Sandrock (consultant)	Nancy Yang

This presentation does not contain any proprietary information.

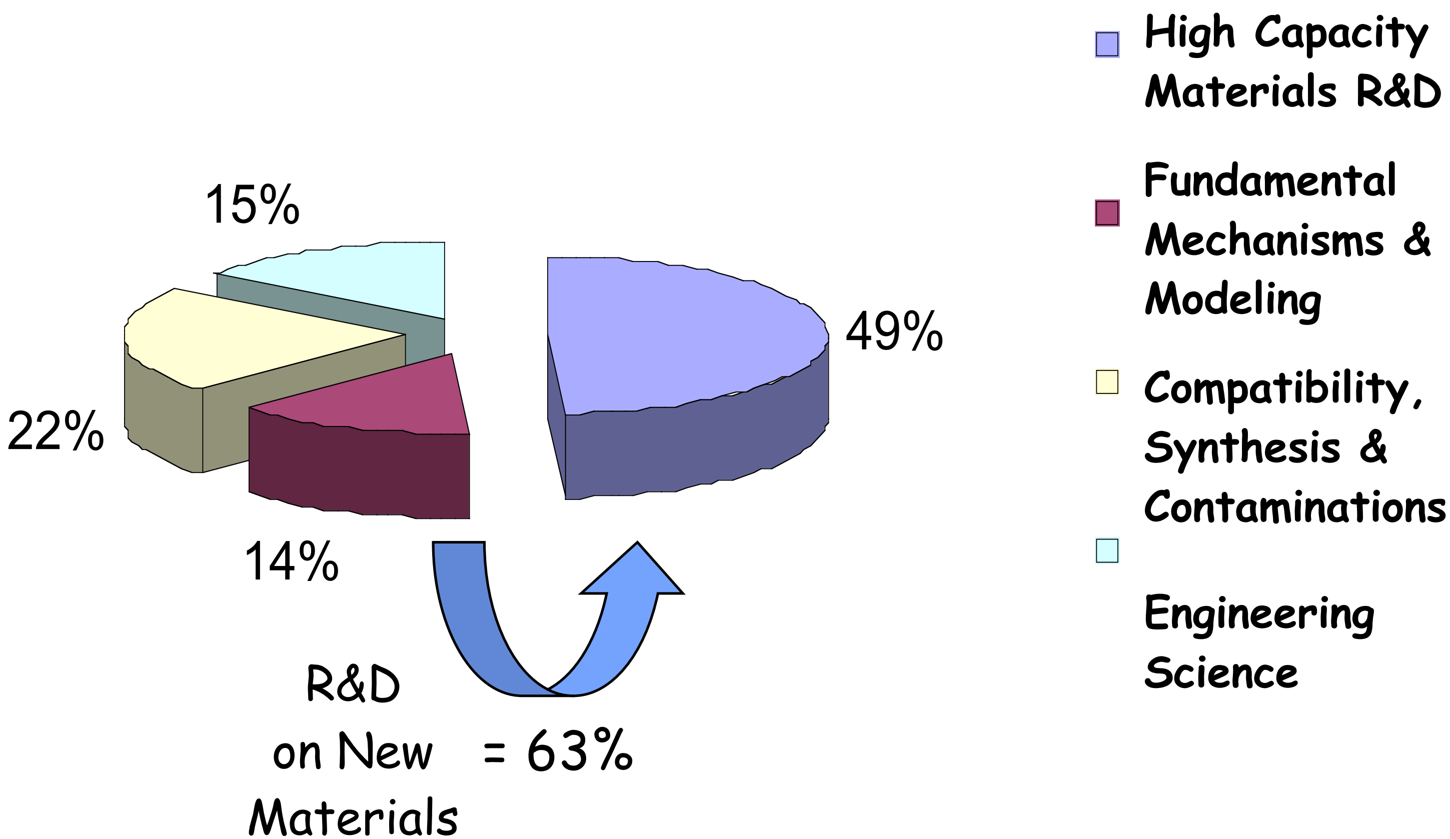
Objective: Meet/Exceed DOE 2010 FreedomCAR on-board hydrogen storage targets



Approach: Science-based Materials Development

Budget

- FY04 Materials R&D Funding $1,700K



Technical Barriers and Targets

- **DOE Technical Barriers for Reversible Solid-State Material Hydrogen Storage Systems**
  - Inadequate hydrogen capacity and reversibility
  - Un-demonstrated materials cycle-life
  - Lack of understanding of hydrogen physisorption and chemisorption
  - Lack of standard test protocols and evaluation facilities
  - Un-defined dispensing technology
- **DOE Technical Target for Reversible Solid-State Hydrogen Storage System in 2010**
  - 6 wt.% minimum reversible hydrogen stored per system
  - Refueling rate at 1.5 Kg H_2 per minutes

Project Safety

Equipment and experimental work:

- Experiments follow Standard Operating Procedures (SOPs)
- All equipment calibrated and can be traced to NIST standards
- Laboratory safety issues are reviewed in full group biweekly meetings

Lessons learned:

- Sodium-alanates are air and water sensitive
- Procedures established for proper preparation and handling, storage and disposal of sodium-alanate materials

Insights and Management of Safety issues:

- Actively participates in DOE H_2 Safety, Codes and Standards program
- Studied interaction of alanates with container vessel materials
- Sponsored alanate safety testing by Thiokol Corp
- Exchange safety information with other researchers in the hydrogen community

Project Timeline

2004 — Q3 — Q4 — 2005 — Q1 — Q2

- PCT & Performance Analysis of Amides
- High Temp & Pressure Synthesis of New Complex Hydrides
- Complete Initial Thermal Properties of Amides
- Large Batch Production of Alanates
- Complete Initial Reversible Borohydride Studies
- Complete Initial Contamination Studies
- Complete Initial Alanates Modeling
- Complete Initial Substituted Li-Amide Studies
- Optimized Non-reactive doping
- Long-term Cycle-Life Measurements
- Initial Modeling of Substitution Mechanism in Amides
- Continue New Hydrogen Storage Materials Exploration

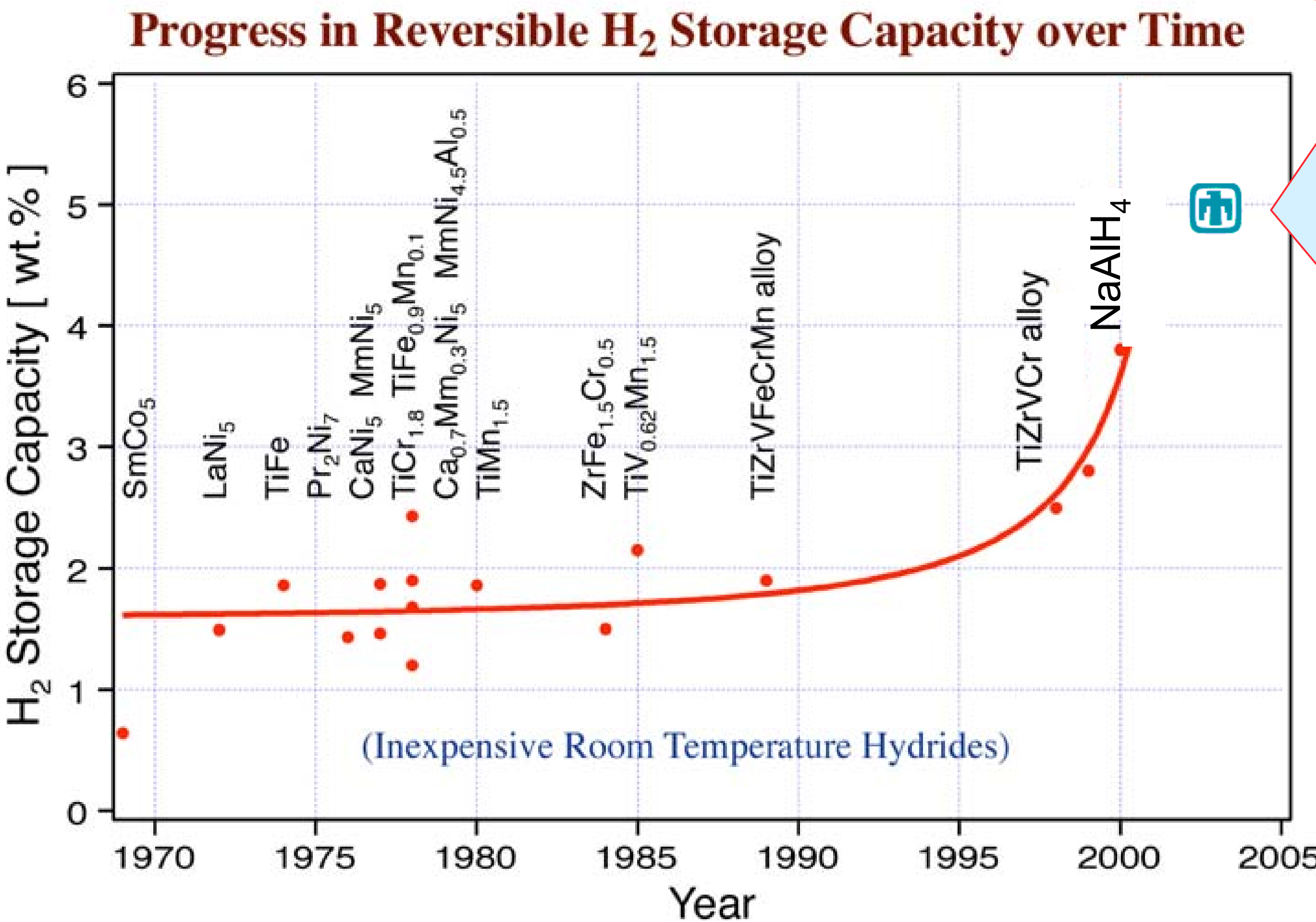
Technical Accomplishments

1. High Capacity Storage Materials Research

- Developed Mg modified Li-amide providing reversible 5 wt% hydrogen storage at 700 psi below 200C with potential for up to 10.4 wt% if the second reaction step is included.
- A new high temperature/ high pressure hydrogen test facility had been assembled and tested for new alanates development.
- Facility at BNL has been established to study the feasibility of decreasing the stability of NaBH4 for reversible reactions.

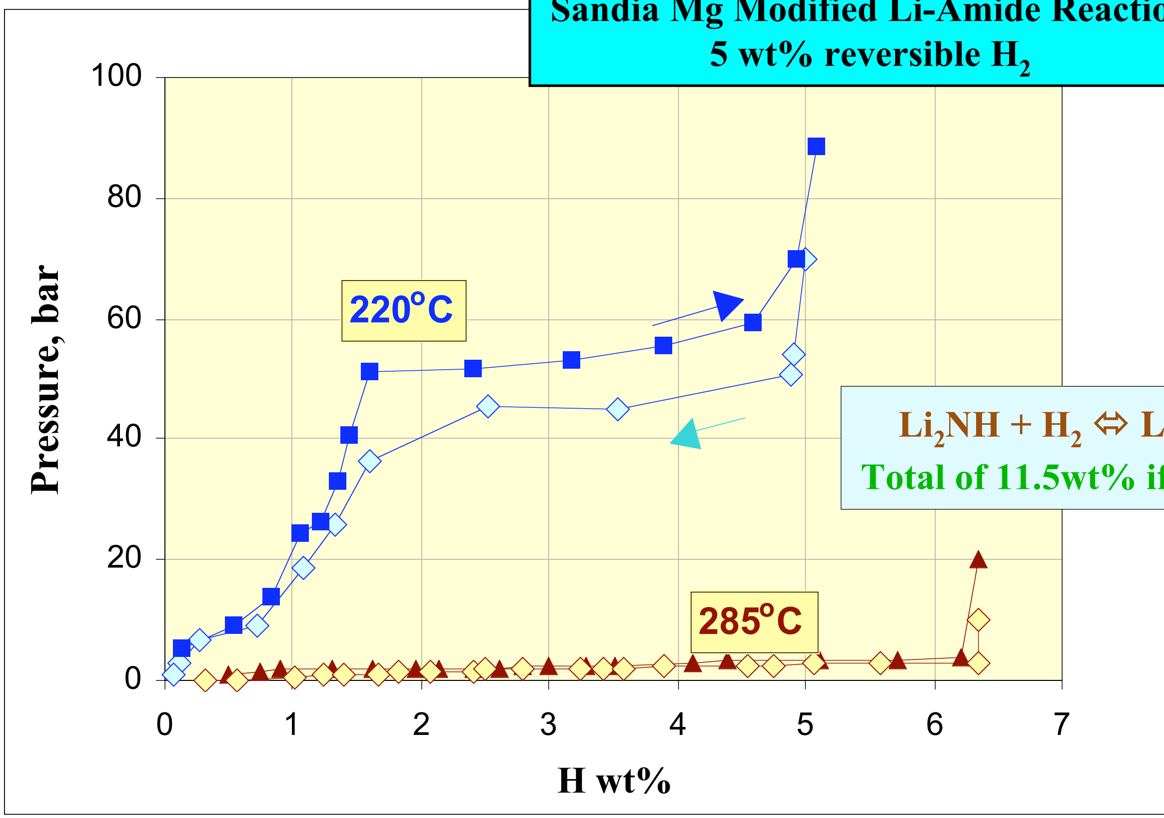
New Complex Hydrides (Progress @ Sandia)

Modified Li Amides with Mg ~ 5wt%



New Complex Hydrides (P-C-T Diagram)

Sandia Mg Modified Li-Amide Reaction
5 wt% reversible H_2

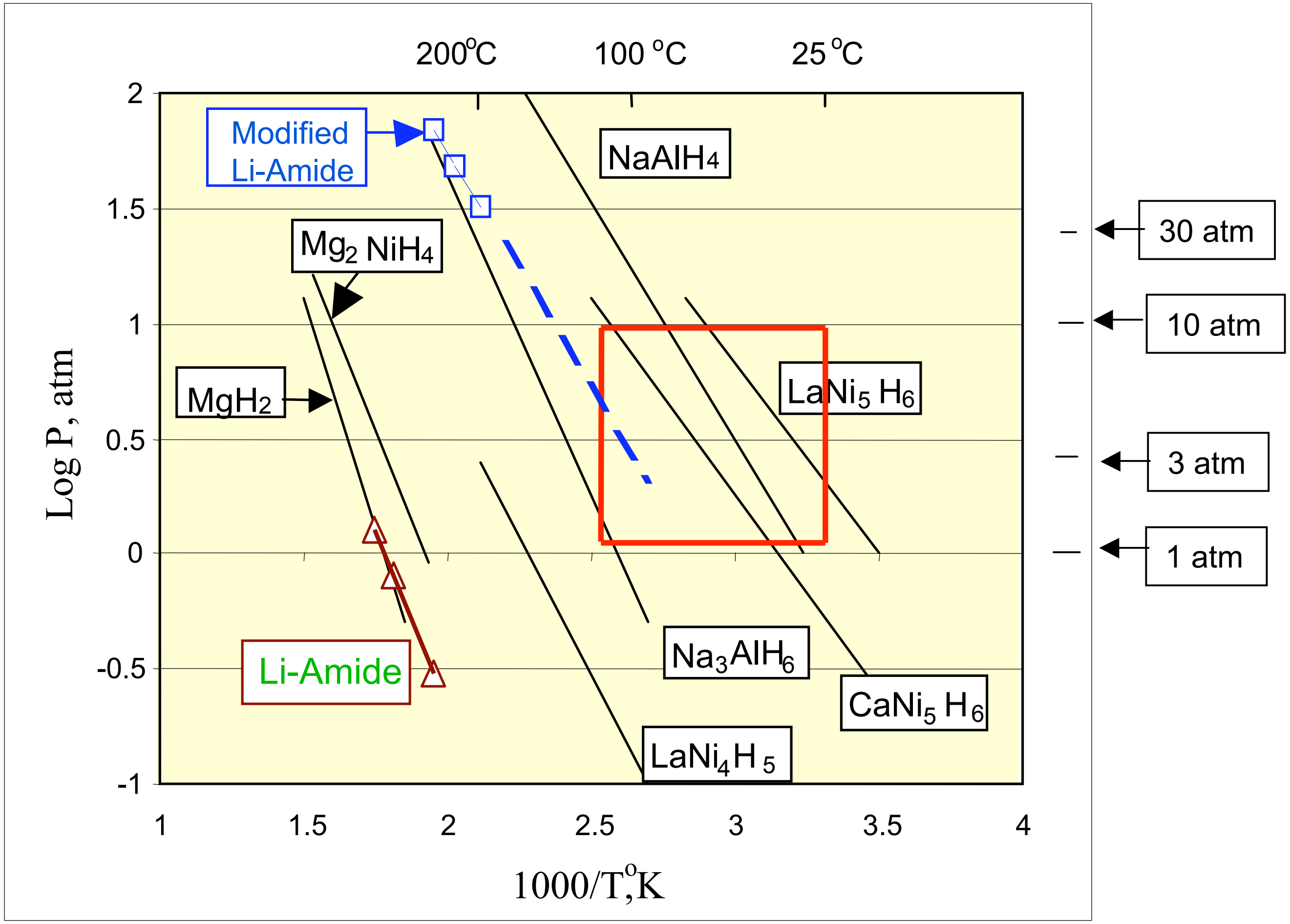


$Li_2NH + H_2 \Leftrightarrow LiNH_2 + LiH$ (6.5wt%)
Total of 11.5wt% if 2nd reaction is included*.

* P. Chen et al, Nature, 420, 21 (2002) 302

Improved lithium amide operating conditions at lower temperature and higher pressure

New Complex Hydrides (Van't Hoff Plot)



Mg modified Li-amides by SNL have potential to meet DOE targets

Search for New Alanates (Material Synthesis Equipment)

- Higher pressure and higher temperature Capabilities

Test Cell capabilities:

Hydrogen pressure up to 30,000 psig

Temperature control up to 700 C

Cell door can be locked for safety

High-Temperature High-Pressure Hydride lab has been developed and assembled for new alanates development

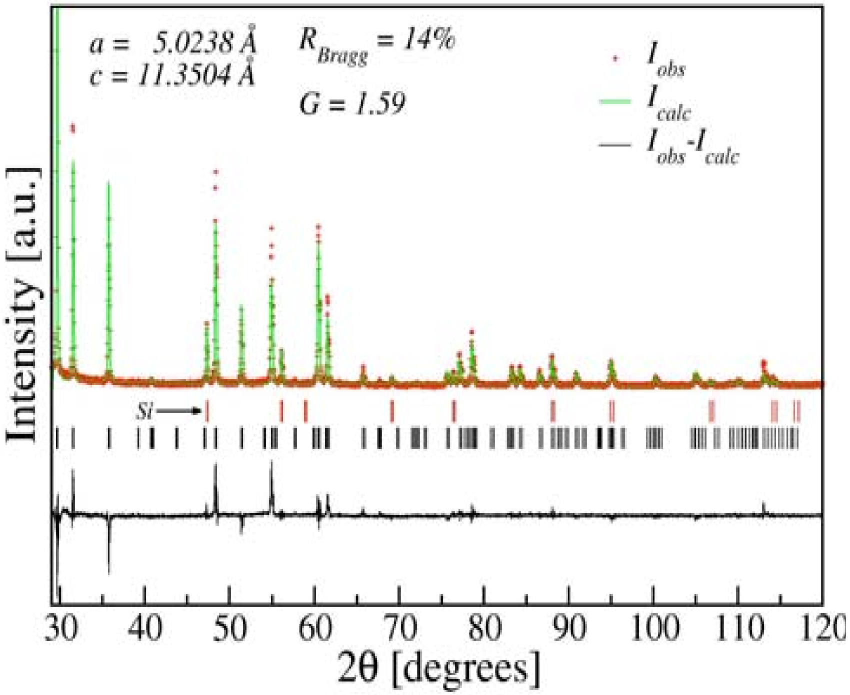
Technical Accomplishments *(cont'd)*

2. Structure Properties and Modeling

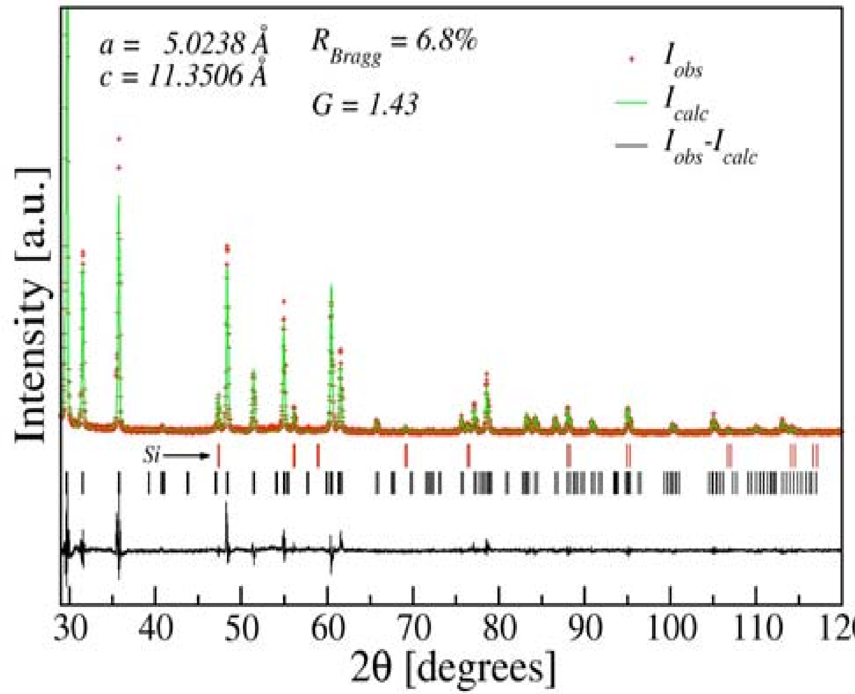
- Demonstrated that Ti did not incorporate into the lattice of Ti exposed $NaAlH_4$ single crystal materials.
- Gained insight from modeling of the role of Ti in hydrogen sorption process on Al surfaces.
- Experimentally verified mass transport of AlH_x in Na alanate reversible reactions.

Ti-doped Sodium Alanates (Structure Properties)

XRD Rietveld refinement of pure and 'Ti exposed' NaAlH4 using NIST Si standard reference.



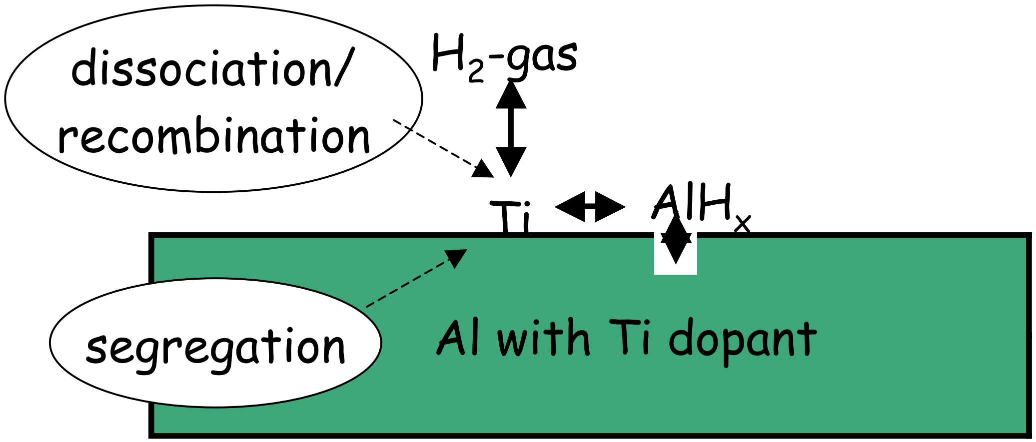
Crystals of pure $NaAlH_4$ from THF



Crystals of $NaAlH_4$ exposed to Ti during growth from THF

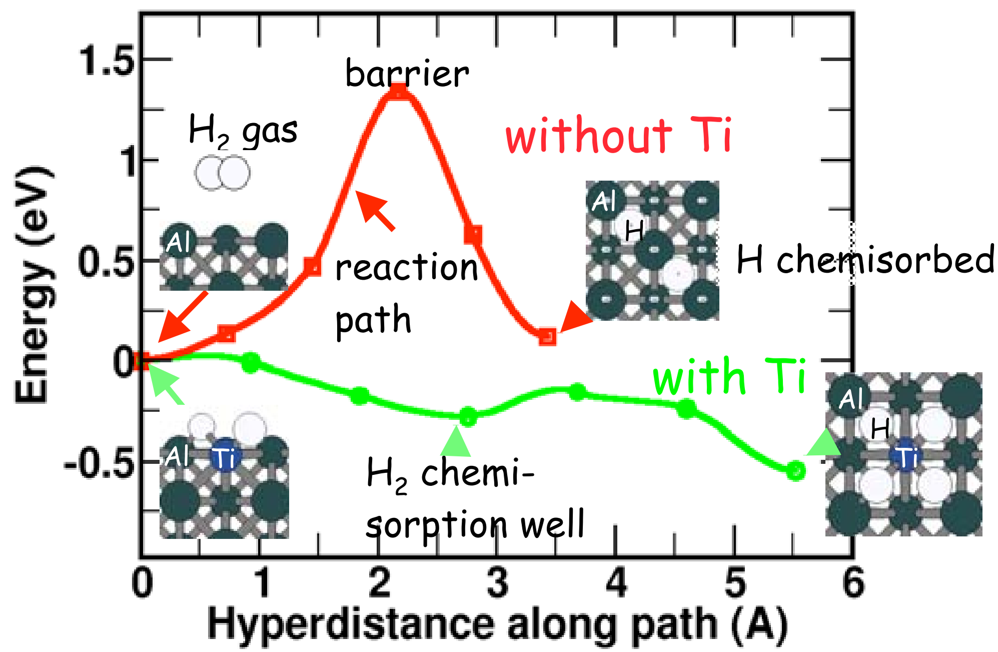
X-ray diffraction shows no evidence of Ti incorporation in the lattice when doped by this method

Ti-doped Sodium Alanates (Fundamental Mechanisms)



First principles calculations (VASP):

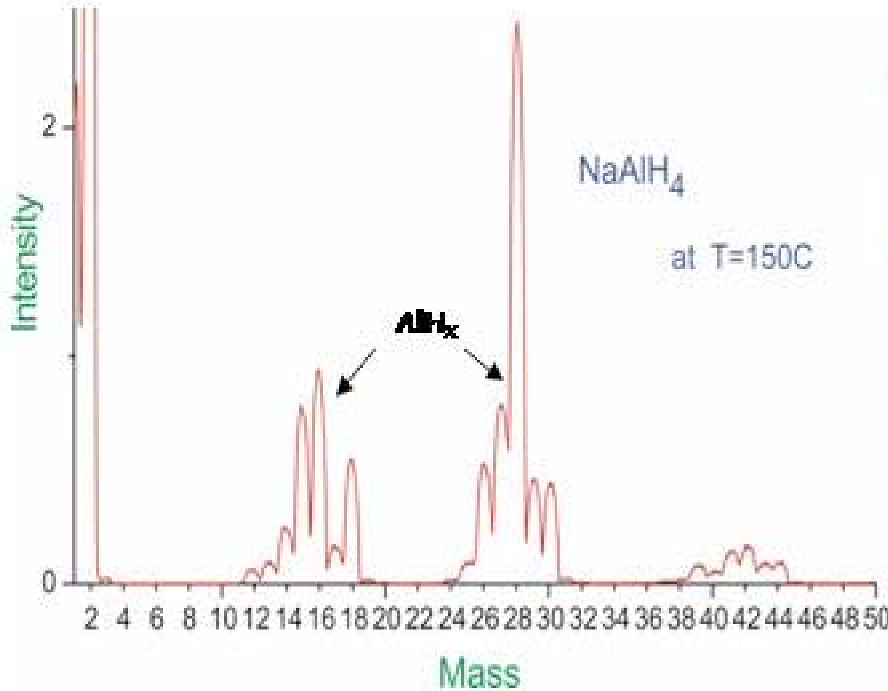
- H adsorption stabilizes Ti at Al and Al_3Ti surfaces
- Ti reduces H_2 sorption barriers at Al surfaces



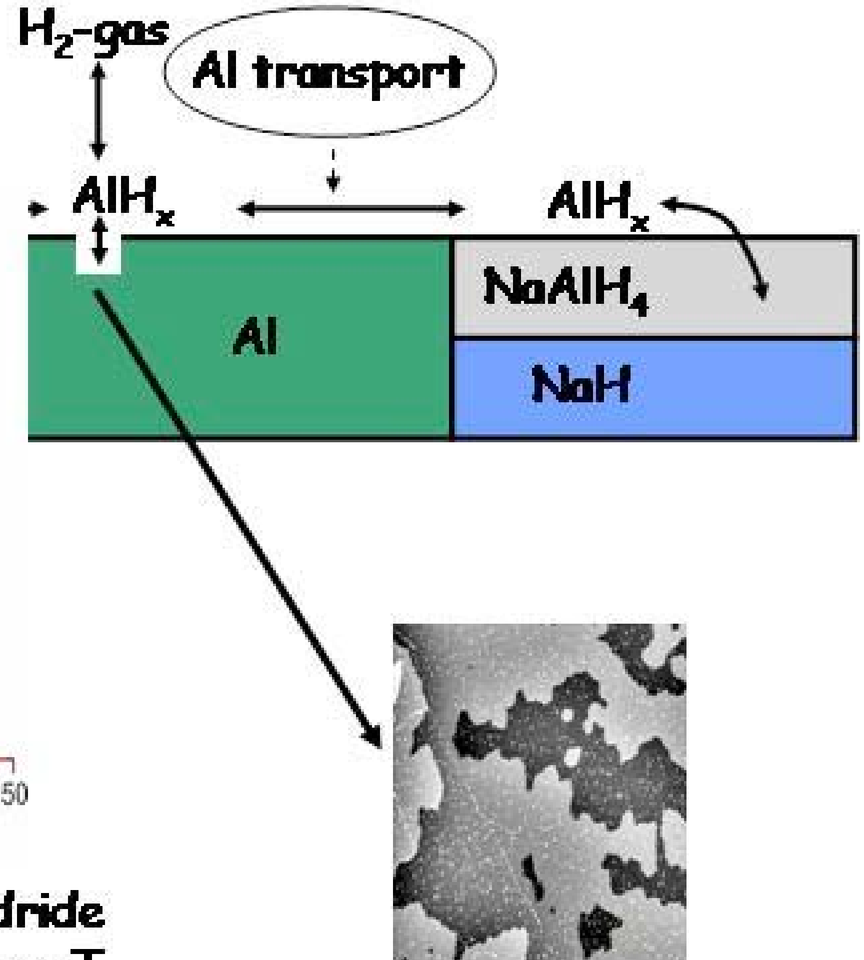
Ti activates H sorption at Al surface

Ti-doped Sodium Alanates (Fundamental Mechanisms)

Thermal Desorption Spectroscopy of Na-alanate



Strong signal from AlH_x species => Al-hydride is volatile at 150C and likely mobile at lower T



STM picture of Al surface pitted in hydrogen environment

Al mass transport likely by AlH_x

Technical Accomplishments *(continued)*

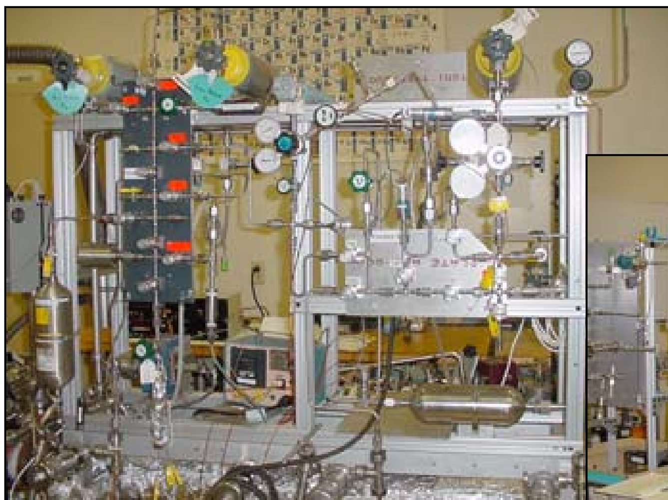
3. Compatibility, Synthesis, Contamination Studies & New Capabilities

- A wet chemistry nano-materials synthesis facility has been established and is ready for nano-sodium alanate and lithium amide materials production.
- Methods using IR spectroscopy are being developed to monitor the effects of contaminants
- New kinetic, P-C-T and cycle-life instruments added to the existing capabilities.

Extensive Experimental Capabilities Added

Hydride labs are being expanded

- 2 cycle life instruments
- 2 air-less sample preparation stations
- 5 manual kinetics systems (including 3 new ones)
- 1 automated PCT instrument
- In situ XRD system



High-pressure kinetics stations

In situ XRD: Full Scans < 1 minute
leverages DP funding

Fully automated PCT instrument

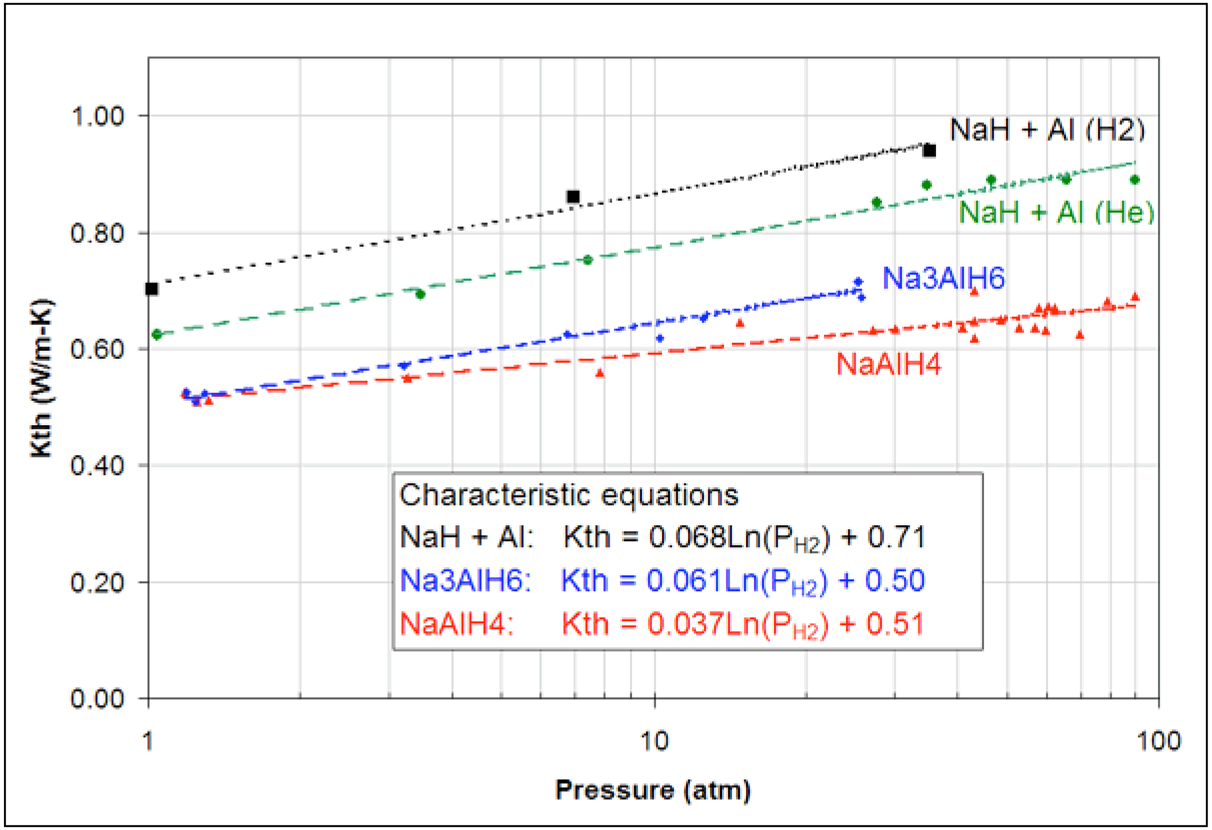
Technical Accomplishments (continued)

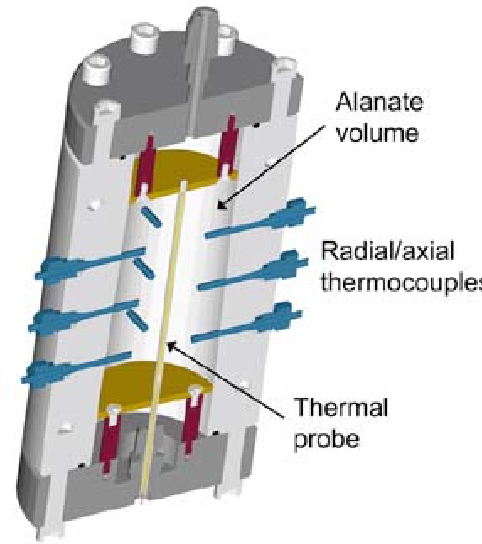
4. Materials Engineering Properties

- Measurements of thermal conductivity, packing density, and expansion of sodium alanates has been completed.

- An empirical predictive model to optimize pressure and temperature for charging & discharging of hydrogen from alanates has been developed to aid in scaled up operating conditions.

Engineering Properties (Thermal Conductivity)

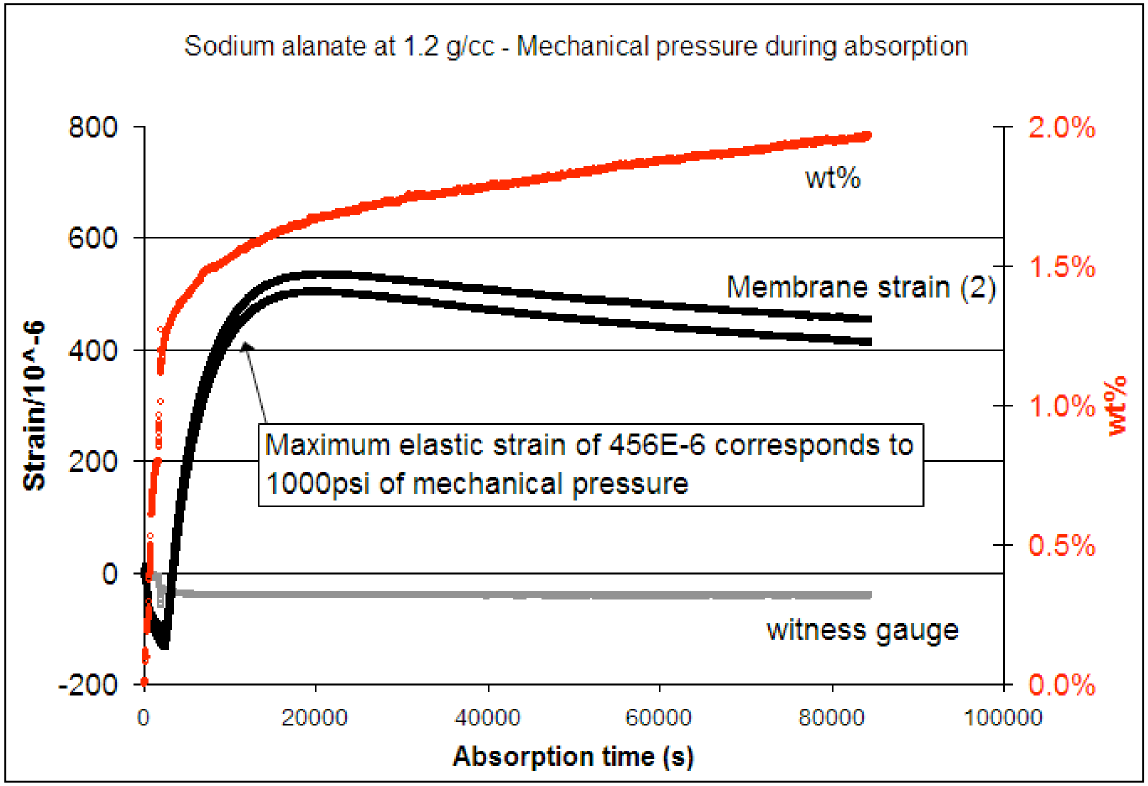


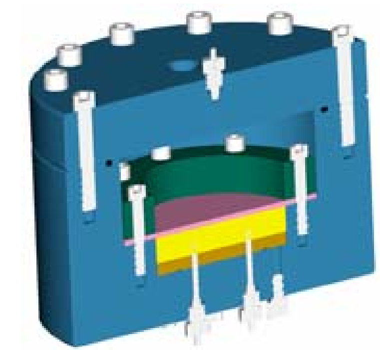


Properties relevant for 3 wt% alanate

Low thermal conductivity of sodium alanate will be a design challenge for H_2 storage systems.

Engineering Properties (Container Wall Pressure)





Initial data:

Density (g/cc)	Wt%*	Pressure (psia)*
0.9	2.4	100
1.2	2.3	1000

*Maximum wt% and pressure attained during experimental set

Higher pressure will be expected for alanate storage systems at high H_2 wt% and high packing densities.

Engineering Properties (Empirical Modeling)

$NaH + 1/3\ Al + \_\ H_2 \Leftrightarrow 1/3\ Na_3AlH_6$
$1/3\ Na_3AlH_6 + 2/3\ Al + H_2 \Leftrightarrow NaAlH_4$

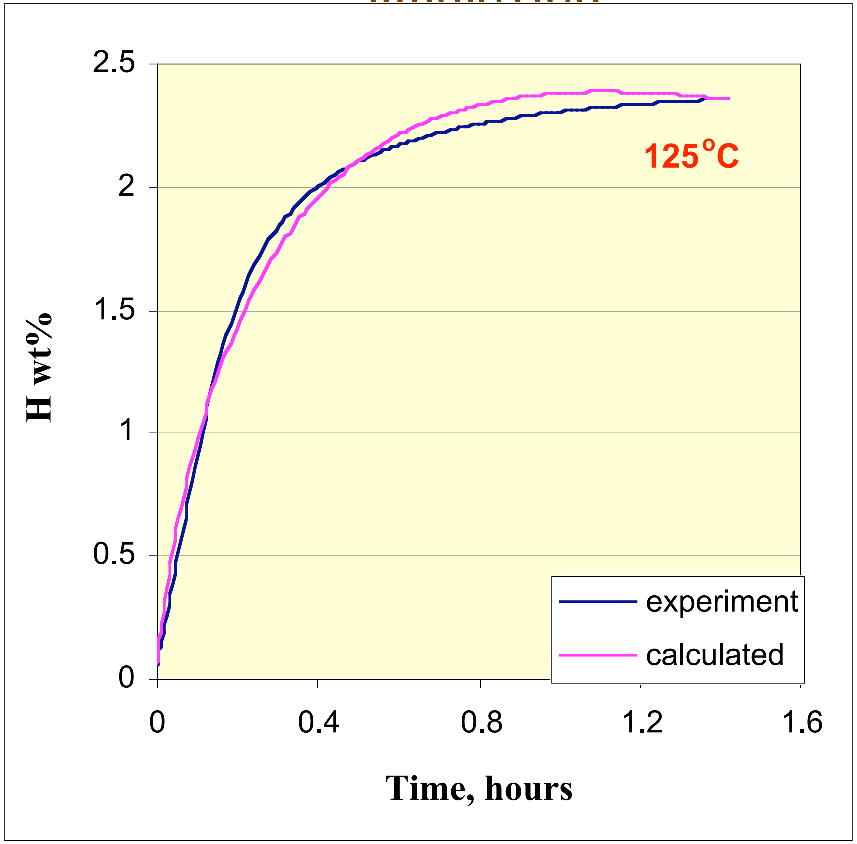
$\text{Rate} = k * F(C) * F(P)$

$$\text{Rate} = k * C^n * b * \ln(P/P_{eq})$$

$n = 1$ or 2;
$b = 1$ or -1;
C: H-wt %;
$k = k_o \exp(-Q_a/RT)$
k: rate constant;
k_o: pre-exponential factor;
Q_a: activation energy

P_{eq}: From K. Gross, Appl. Physics, 2001. (Van't Hoff plot).
No hysteresis was considered.

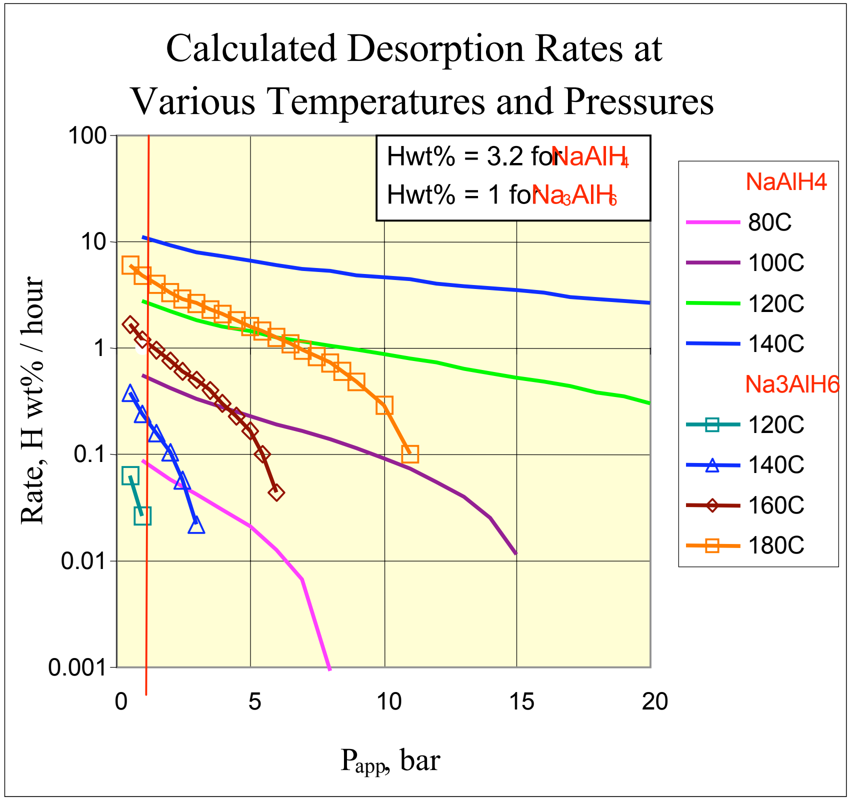
Alanate Desorption Simulation



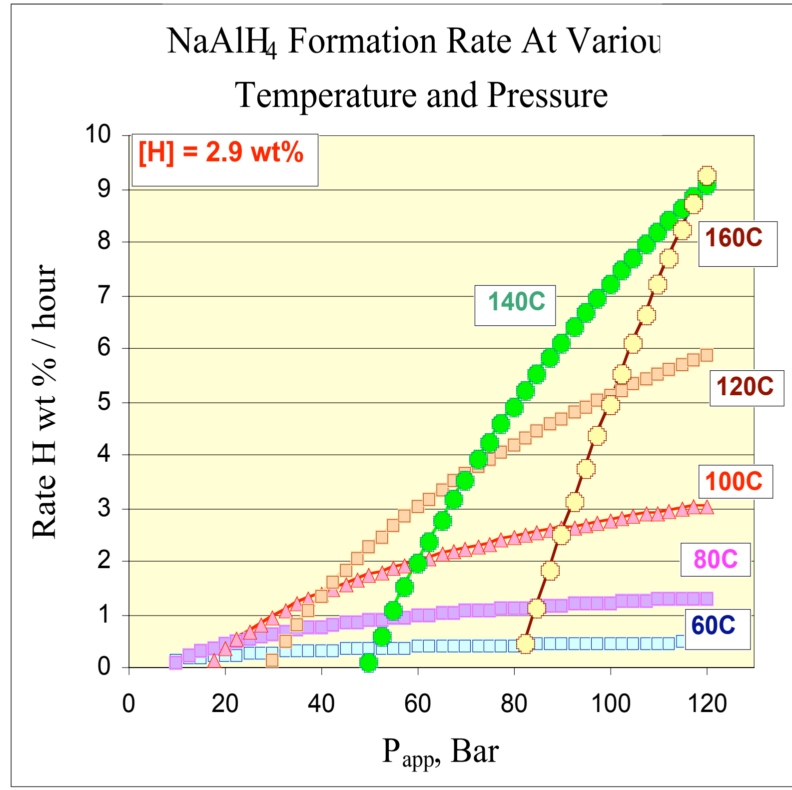
An empirical charging/discharging kinetic model has been developed

Engineering Science (Empirical Modeling continued)

Discharge estimation



Charge optimization



This model can be used to optimize storage system design

Interactions and Collaborations

University of Hawaii: Mechanisms of Ti-doping enhanced kinetics

University of Geneva (IEA): New Complex Hydrides

Tohoku University (IEA): Li-Amides Characterization

University of Singapore: Li-Amides Synthesis and Performance

Brookhaven National Laboratory – Reversible Borohydrides

Denver University: Electron Spin Resonance measurements

Lawrence Livermore: Solid-State Nuclear Magnetic Resonance

NIST: Neutron Diffraction and Scattering Spectroscopy

UCLA: Ab Initio Calculations

UTRC: Materials Purity Issues and Safety Testing

Response to previous Year' Reviewers' Comments

1. ***Many positive comments*** - Our approach validated
2. ***Need to expand materials search***
   - More than 60% budget on new materials R&D in FY04
   - Exciting results from modified lithium amides
3. ***More basic science needs to be done***
   - Added more expertise in modeling, surface science and reaction chemistry in FY04
4. ***More thermodynamics to investigate Ti-doping***
   - Measurements are currently underway
5. ***Extend collaborations and team work***
   - Focus and strength of our DOE Metal Hydride virtual Center of Excellence.
6. ***Continue engineering materials investigation***
   - Much progress made and ongoing

Future Plans

- **Remainder of FY2004:**
  - *Lithium amide materials research and development*
    - Optimize capacity and kinetics via experiments and modeling
    - Measure mechanical and heat transfer properties
    - Evaluate safety and contamination effects
    - Develop new synthesis route for nano-materials productions
  - *Other new complex hydrides*
    - Synthesize new hydride materials using high T & P facilities
    - Evaluate properties and performance of new materials
    - Understand mechanisms of Ti doped alanates via modeling and characterizations, especially of surface reactivity aspects
    - Study safety and contamination effects on alanates
- **FY2005 and beyond:**
  - *Lead the DOE Center of Excellence on Metal Hydrides focusing on optimizing present materials and developing new hydrogen storage materials to meet/exceed DOE FreedomCAR 2010 targets*

Proposed DOE Metal Hydride virtual Center of Excellence (MHvCE)

DOE
Office of Hydrogen, Fuel Cells & Infrastructure Technologies

MHvCE
Management Team
(Jim Wang, Jay Keller, Karl Gross)

Management Advisory Committee

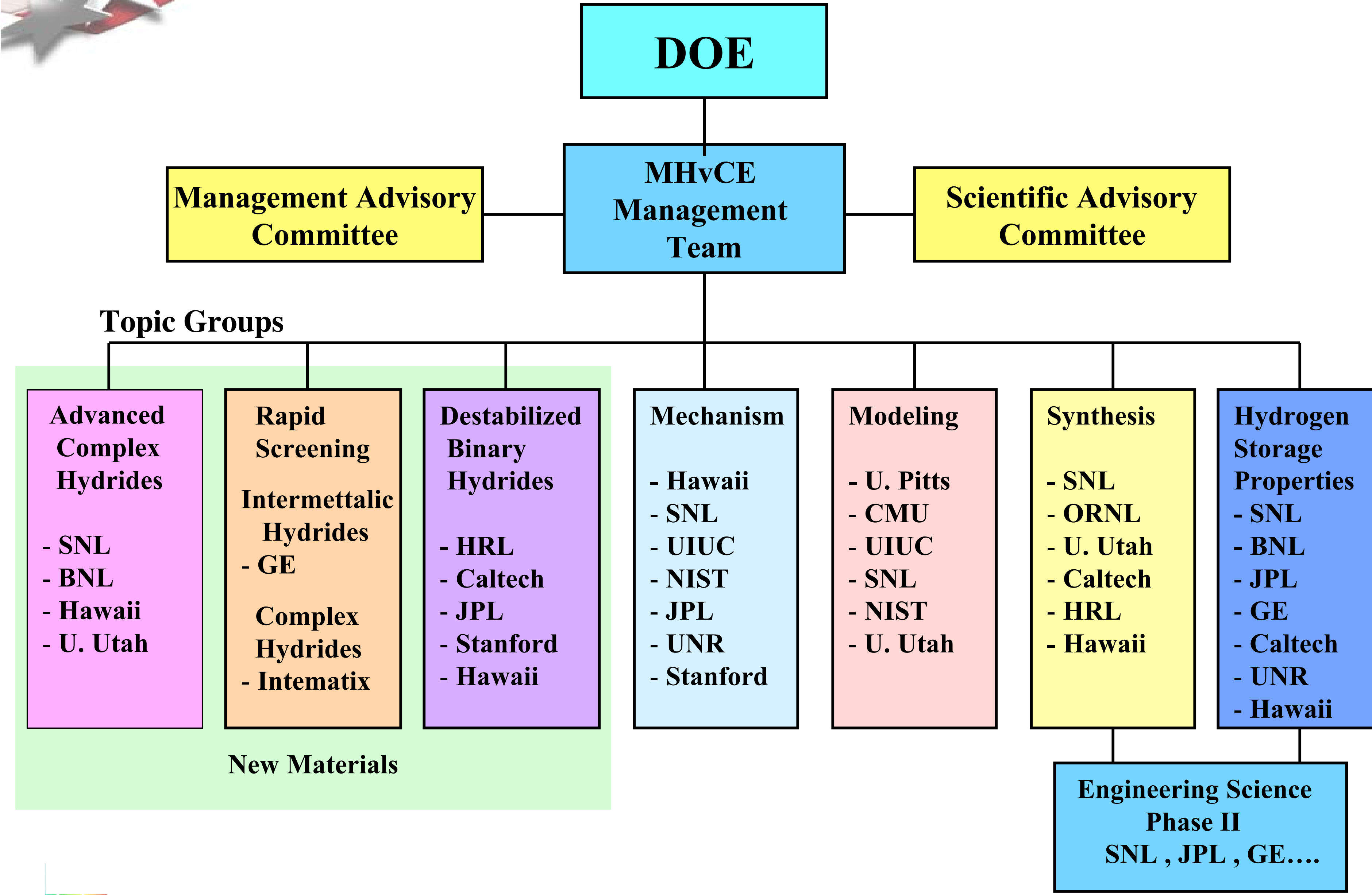
Scientific Advisory Committee

Sandia as MHvCE Lead Lab
12 Tasks including new hydrides synthesis, characterization, performance testing, fundamental modeling, engineering properties, and Center management

8 Universities
(Hawaii, Pittsburgh, Carnegie Mellon, Illinois, Caltech, Stanford, Utah, UN-Reno)

3 Industrial Companies
(GE, HRL, Intematix)

4 Other National Labs
(BNL, ORNL, JPL, NIST)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MHvCE Management Team
Management Advisory Committee
Scientific Advisory Committee
Topic Groups
Advanced Complex Hydrides
- SNL
- BNL
- Hawaii
- U. Utah
Rapid Screening
Intermettalic Hydrides
- GE
Complex Hydrides
- Intematix
Destabilized Binary Hydrides
- HRL
- Caltech
- JPL
- Stanford
- Hawaii
Mechanism
- Hawaii
- SNL
- UIUC
- NIST
- JPL
- UNR
- Stanford
Modeling
- U. Pitts
- CMU
- UIUC
- SNL
- NIST
- U. Utah
Synthesis
- SNL
- ORNL
- U. Utah
- Caltech
- HRL
- Hawaii
Hydrogen Storage Properties
- SNL
- BNL
- JPL
- GE
- Caltech
- UNR
- Hawaii
New Materials
Engineering Science Phase II
SNL , JPL , GE….

Acknowledgement

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